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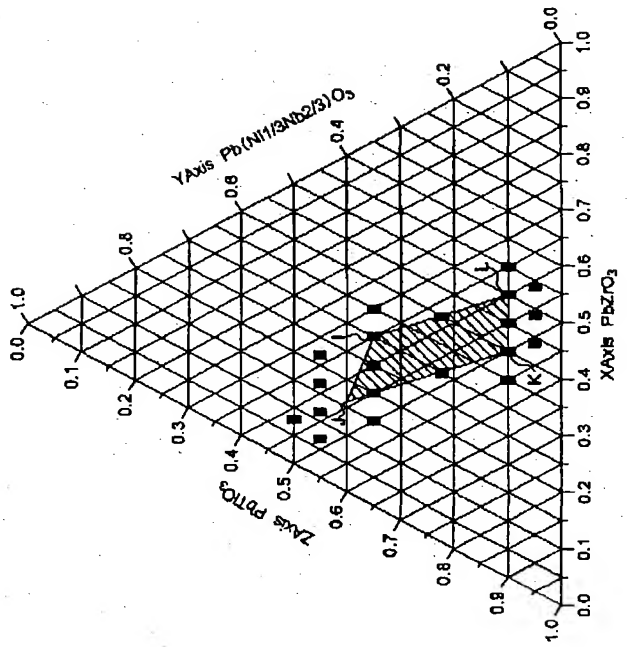
最終頁に続く

(54)【発明の名称】圧電磁器組成物

(57)【要約】
【課題】　特に高電界下での圧電変位量が大きく，且つ比誘電率の温度変化が小さいとともに，絶縁性に優れた圧電磁器材料を提供する。
【解決手段】　圧電磁器組成物は、組成式ａＰｂＴｉＯ$_3$＋ｂＰｂＺｒＯ$_3$＋ＣＰｂ（Ｎｉ$_{1/3}$・Ｎｂ$_{2/3}$）Ｏ$_3$　（ａ＋ｂ＋ｃ＝１００）で表され，その組成範囲が，図１のＩ点（ａ＝３５ｍｏｌ％，ｂ＝３０ｍｏｌ％，ｃ＝３５ｍｏ・％），Ｊ点（ａ＝４４ｍｏｌ％，ｂ＝１６ｍｏｌ％，ｃ＝４０ｍｏｌ％），Ｋ点（ａ＝５０ｍｏｌ％，ｂ＝４０ｍｏｌ％，ｃ＝１０ｍｏｌ％），Ｌ点（ａ＝４０ｍｏｌ％，ｂ＝５０ｍｏｌ％，ｃ＝１０ｍｏｌ％）の組成点を結ぶ線上およびこの４点に囲まれた領域とする範囲であり，分極軸と同一方向に，５００ｋＶ／ｍの直流電界を印加したときの圧電変位が５００ｐｍ／Ｖ以上となり，かつ，－４０℃～１７０℃の範囲で，比誘電率の温度変化が３００％以下である。



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【特許請求の範囲】

【請求項１】　組成式ａＰｂＴｉO_3＋ｂＰｂＺｒO_3＋ｃＰｂ（Ｎｉ$_{1/3}$・Ｎｂ$_{2/3}$）O_3（ａ＋ｂ＋ｃ＝１００）で表され，その組成範囲が，図１に示すＩ点（ａ＝３５ｍｏｌ％，ｂ＝３０ｍｏｌ％，ｃ＝３５ｍｏｌ％）、Ｊ点（ａ＝４４ｍｏｌ％，ｂ＝１６ｍｏｌ％，ｃ＝４０ｍｏｌ％）、Ｋ点（ａ＝５０ｍｏｌ％，ｂ＝４０ｍｏｌ％，ｃ＝１０ｍｏｌ％）、Ｌ点（ａ＝４０ｍｏｌ％，ｂ＝５０ｍｏｌ％，ｃ＝１０ｍｏｌ％）の各組成点を結ぶ線上およびこの４点に囲まれた領域とする範囲であり，分極軸と同一方向に，５００ｋＶ／ｍの直流電界を印加したときの圧電変位ｄ３３（５００ｋＶ）が，５００ｐｍ／Ｖ以上となり，かつ，－４０℃～１７０℃の範囲で，比誘電率の温度変化が３００％以下であることを特徴とする圧電磁器組成物。

【請求項２】　請求項１記載の圧電磁器組成物において、更に、圧電磁器組成物の総量に対して，ＭｎをＭｎＯで表される酸化物に換算して，０～０．０５ｗｔ％（０は含まず）の割合で含有し，－４０℃～１７０℃における比抵抗が１．０×10^{11}Ω・ｃｍ以上であることを特徴とする圧電磁器組成物。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、チタン酸ジルコン酸鉛を主成分とする圧電磁器組成物に関するものであり，特に高電界下での圧電変位量が大きく，且つ比誘電率の温度変化が小さいとともに，絶縁性に優れた圧電磁器組成物に関するものである。

【０００２】

【従来の技術】従来、圧電磁器材料としては，ＰｂＴｉO_3やＰｂＺｒO_3を主成分として含む圧電セラミックス（以下，ＰＺＴ系圧電セラミックスと呼ぶ）や，複合ペロブスカイト類を第三，第四成分として固溶させた多成分系ＰＺＴ系圧電セラミックスが，圧電定数が大であるために，圧電振動子を初めとしてアクチュエータ用の材料として広く利用されている。これらの系の圧電磁器材料は，一般にモルフォトピック相境界（ＭＰＢ）近傍組成において，圧電定数（ｄ定数）等の圧電変位に寄与する特性が向上するため，アクチュエータ用材料には，ＭＰＢ近傍組成の圧電磁器材料が広く実用化されている。

【０００３】

【発明が解決しようとする課題】しかしながら，前記圧電定数は、一般にＥＭＡＳ－６１００等で示された，共振－反共振法で求められた値であり，基本的には低電界（約数百Ｖ／ｍ程度）印加時の圧電変位の割合を示している。これに対し，実際の圧電アクチュエータにおける駆動電界は，数百ｋＶ／ｍ～数千ｋＶ／ｍにもなり，前記方法で求めた圧電定数が実用的な意味を持たない場合がある。

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【０００４】さらに、近年、圧電アクチュエータ利用範囲の広がりにともない，広い温度範囲での特性安定性，特に静電容量の温度安定性が求められている。例えば，自動車用部品として圧電アクチュエータが使用される場合には，その使用環境に応じて，－４０℃～１７０℃にもなる広い温度範囲での特性安定性が要求される場合がある。これに対し，一般に前記ＭＰＢ近傍組成での圧電磁器材料は，比誘電率の温度変動が大きくなり，広い温度範囲におけるアクチュエータ特性の安定性，特に静電容量の安定性に問題が生じている。ＰｂＴｉO_3－ＰｂＺｒO_3－Ｐｂ（Ｎｉ$_{1/3}$Ｎｂ$_{2/3}$）O_3系（以下，ＰＮＮ－ＰＺＴ系と呼ぶ）の圧電磁器組成物はｄ定数が大きいため，アクチュエータ素子用の圧電磁器材料として利用されている。しかし，この系の圧電磁器材料は電気抵抗率が比較的小さく，積層型圧電素子のように一層の厚みが１００μｍ前後の素子に使用した場合，印加できる電圧を大きくできず，充分な特性を引き出せなかったり，使用中に絶縁破壊してしまう等の問題点が生じている。

【０００５】また，前記ＰＮＮ－ＰＺＴ系圧電磁器材料は，電気抵抗率の温度変動も大きいため，特に前述のような広い温度範囲で使用する場合には，さらに信頼性が低下するなどの問題があった。

【０００６】そこで、本発明の一般的な技術的課題は、高電圧印加時の圧電歪定数が大きく，かつ，比誘電率の温度変化が小さく，高温度範囲での電気抵抗率も大きいことから，広い温度範囲で安定な特性を有する圧電磁器組成物を提供することにある。

【０００７】また、本発明の特別な技術的課題は、前記圧電磁器組成物から実質的になり、アクチュエータ用材料として有用な圧電磁器組成物を提供することにある。

【０００８】

【課題を解決するための手段】本発明者は，組成式ａＰｂＴｉO_3＋ｂＰｂＺｒO_3＋ｃＰｂ（Ｎｉ$_{1/3}$Ｎｂ$_{2/3}$）O_3（ａ＋ｂ＋ｃ＝１００）で表される圧電磁器組成物の圧電変位特性を種々調査した結果，その組成範囲が，所定の領域でｄ３３（５００ｋＶ）が，５００ｐｍ／Ｖ以上となり，かつ，－４０℃～１７０℃の範囲で，比誘電率の温度変化が３００％以下となることを見出し、本発明を為すに至ったものである。

【０００９】また，上記圧電磁器組成物に対して，ＭｎをＭｎＯで表される酸化物に換算して，０～０．０５ｗｔ％（０は含まない）の割合で含有することにより，上記圧電磁器組成物の絶縁性が向上することを見出し、本発明を為すに至ったものである。

【００１０】即ち、本発明によれば、組成式ａＰｂＴｉO_3＋ｂＰｂＺｒO_3＋ｃＰｂ（Ｎｉ$_{1/3}$・Ｎｂ$_{2/3}$）O_3（ａ＋ｂ＋ｃ＝１００）で表され，その組成範囲が，図１に示すＩ点（ａ＝３５ｍｏｌ％，ｂ＝３０ｍｏｌ％，ｃ＝３５ｍｏｌ％）、Ｊ点（ａ＝４４ｍｏ

ｌ%，ｂ＝１６ｍｏｌ%，ｃ＝４０ｍｏｌ%）、Ｋ点（ａ＝５０ｍｏｌ%，ｂ＝４０ｍｏｌ%，ｃ＝１０ｍｏｌ%）、Ｌ点（ａ＝４０ｍｏｌ%，ｂ＝５０ｍｏｌ%，ｃ＝１０ｍｏｌ%）の各組成点を結ぶ線上およびこの４点に囲まれた領域とする範囲であり，分極軸と同一方向に，５００ｋＶ／ｍの直流電界を印加したときの圧電変位ｄ３３（５００ｋＶ）が，５００ｐｍ／Ｖ以上となり，かつ，－４０℃～１７０℃の範囲で，比誘電率の温度変化が３００%以下であることを特徴とする圧電磁器組成物が得られる。

【００１１】また、本発明によれば、前記圧電磁器組成物において、更に、圧電磁器組成物の総量に対して，ＭｎをＭｎＯで表される酸化物に換算して，０～０．０５ｗｔ%（０は含まず）の割合で含有し，－４０℃～１７０℃における比抵抗が１．０×10^{11}Ω・ｃｍ以上であることを特徴とする圧電磁器組成物が得られる。

【００１２】

【発明の実施の形態】まず、本発明について図面を参照して説明する。

【００１３】図１は本発明の圧電磁器組成物の組成範囲を三角座標で示した図である。図１に示すように、本発明の圧電磁器組成物は、Ｉ点（ａ＝３５ｍｏｌ%，ｂ＝３０ｍｏｌ%，ｃ＝３５ｍｏｌ%），Ｊ点（ａ＝４４ｍｏｌ%，ｂ＝１６ｍｏｌ%，ｃ＝４０ｍｏｌ%），Ｋ点（ａ＝５０ｍｏｌ%，ｂ＝４０ｍｏｌ%，ｃ＝１０ｍｏｌ%），Ｌ点（ａ＝４０ｍｏｌ%，ｂ＝５０ｍｏｌ%，ｃ＝１０ｍｏｌ%）の組成点を結ぶ線上およびこの４点に囲まれた領域とする範囲の組成を有する。この組成において、本発明の圧電磁器組成物は、分極軸と同一方向に，５００ｋＶ／ｍの直流電界を印加したときの圧電変位ｄ３３（５００ｋＶ）が，５００ｐｍ／Ｖ以上となり，かつ，－４０℃～１７０℃の範囲で，比誘電率の温度変化が３００%以下の特性を有するものである。

【００１４】さらに、本発明の圧電組成物は、前記圧電磁器組成物において、更に、圧電磁器組成物の総量に対して，ＭｎをＭｎＯで表される酸化物に換算して，０～０．０５ｗｔ%（０は含まず）の割合で含有し、これによって、－４０℃～１７０℃における比抵抗が１．０×

10^{11}Ω・ｃｍ以上の特性を有するものである。

【００１５】次に、本発明の実施の形態について、説明する。

【００１６】（第１の実施の形態）酸化鉛（ＰｂＯ）、酸化チタン（ＰｂＯ），酸化ジルコニウム（ZrO_2），酸化ニッケル（ＮｉＯ），酸化ニオブ（Nb_2O_5）の原料を，化学式$aPbTiO_3-bPbZrO_3-cPb(Ni_{1/3}Nb_{2/3})O_3$となるように秤量し，これらの原料粉をジルコニアボールとともにアクリルポット中に入れ，２０時間湿式混合した。次に，これらの混合粉を脱水乾燥後，アルミナこう鉢中で予焼を行ってから，各予焼粉をアクリルポット中ジルコニアボールにて１５時間湿式粉砕した。引き続き，脱水乾燥して得られた予焼粉砕粉にバインダを混合して加圧し，直径（φ）１５×厚さ（Ｔ）３ｍｍに成形した。この成形体を１１００℃～１３００℃で２時間焼成し，各焼結体を１ｍｍの厚さに加工した後，両面に銀ペーストを塗布して４５０℃で焼き付けて電極を形成することにより，それぞれ組成の異なる試料とした。このようにして得られた各試料を３ｋＶ／ｍｍで分極処理をし，ＨＰ４１９４Ａと恒温槽を使用して，１ＫＨｚの比誘電率εrの温度特性を測定した。温度特性は，－４０℃～４００℃の範囲で５℃～１０℃毎に３０分保持したのち，各温度での１ＫＨｚのεrを測定した。また，ｄ３３（５００ＫＶ）は，中心点で支持した前記試料に，等速，２秒間で０Ｖ→５００Ｖ→０Ｖの電圧を印加し，試料厚さ方向の変位をフリンジカウンタ式レーザ変位計を使用して測定して算出した。

【００１７】図２はｄ３３（５００ｋＶ）の測定例を示す図である。図２に示すように，厚さ１ｍｍの測定試料に，５００Ｖの直流電圧印加時（電界強度５００ｋＶ／ｍ）の変位量からｄ３３（５００ＫＶ）を算出した。

【００１８】また、下記表１に，各組成点でのｄ３３（５００ＫＶ）と，－４０℃～１７０℃のでのεrの温度変化率を示す。表１中「＊」を付した試料Ｎｏ．は，本発明の範囲外を示している。

【００１９】

【表１】

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各組成点における圧電磁器材料の特性

	試料No.	各成分			d_{33}(500KV)/pm・V^{-1}	Δεr	Tc(℃)
		a	b	c			
*	1	43	12	45	530	500%	180
	2	44	16	40	670	170%	200
*	3	39	21	40	1250	550%	190
*	4	50	15	35	450	170%	230
	5	45	20	35	530	180%	220
	6	40	25	35	1000	230%	210
	7	35	30	35	800	280%	200
*	8	30	35	35	700	700%	190
	9	47.5	30	22.5	520	160%	270
	10	37.5	40	22.5	750	290%	250
*	11	55	35	10	470	150%	340
	12	50	40	10	520	180%	330
	13	45	45	10	700	170%	320
	14	40	50	10	600	270%	310
*	15	35	55	10	520	700%	300
*	16	51	44	5	420	160%	350
*	17	46	49	5	480	190%	340
*	18	41	54	5	400	280%	330

備考）＊印は本発明の範囲外

上記表１より，以下の事が読み取れる。すなわち，試料Ｎｏ．１，３，８においては，圧電磁器組成物のキュリー温度（Ｔｃ）が２００℃以下となり，－４０℃～１７０℃でのεｒの温度変化が３００％を超えるので，本発明の範囲に含まれない。

【００２０】また，試料Ｎｏ．７，１０，１４を結ぶ線よりも，ＰｂＺｒＯ$_3$リッチな領域では，比較的高いｄ３３（５００ｋＶ）が得られているにも関らず，εｒの温度変化が極めて大きくなるため，本発明の範囲に含まれない。

【００２１】また，試料Ｎｏ．４，１１，１６，１７，１８は，それぞれｄ３３（５００ｋＶ）の値が，５００ｐｍ／Ｖ未満となるため，本発明の範囲に含まれない。

【００２２】これらの結果から，本発明の目標とする特性は，試料Ｎｏ．２，７，１２，１４の各々，Ｎｏ．２（ａ＝４４ｍｏｌ％，ｂ＝１６ｍｏｌ％，ｃ＝４０ｍｏｌ％），Ｎｏ．７（ａ＝３５ｍｏｌ％，ｂ＝３０ｍｏｌ％，ｃ＝３５ｍｏｌ％），Ｎｏ．１２（ａ＝５０ｍｏｌ％，ｂ＝４０ｍｏｌ％，ｃ＝１０ｍｏｌ％），Ｎｏ．１４（ａ＝４０ｍｏｌ％，ｂ＝５０ｍｏｌ％，ｃ＝１０ｍｏｌ％）の組成点を結ぶ線上およびこの４点に囲まれた領域とする範囲で、図１に示す４角形で囲まれた領域で達成されることがわかる。

【００２３】（第２の実施の形態）酸化鉛（ＰｂＯ），酸化チタン（TiO_2），酸化ジルコニウム（ZrO_2），酸化ニッケル（ＮｉＯ），酸化ニオブ（Nb_2O_5），炭酸マンガン（$MnCO_3$）の原料を化学式ａＰｂＴｉＯ$_3$－ｂＰｂＺｒＯ$_3$－ＣＰｂ（Ｎｉ$_{1/3}$Ｎｂ$_{2/3}$）Ｏ$_3$＋ＭｎＯ（ｗｔ％）となるように秤量し，第１の実施の形態と同じ方法で試料を作成し，作成した試料の－４０℃，１７０℃それぞれでの比抵抗を測定した。

【００２４】その結果の一例を図３に示す。図３から，恒温領域では比抵抗が低下するものの，ＭｎＯを極微量添加するだけで，比抵抗が顕著に向上し，本発明の目標値を満足することがわかる。また，ＭｎＯの添加量は，０．０５ｗｔ％を超えると，それ以上の比抵抗向上効果は望め無いことがわかった。ＭｎＯの過剰な添加は，圧電定数などの圧電特性を劣化させる傾向もあるため，０．０５ｗｔ％以下が，本発明の目標に対して適当な値であると判断できる。

【００２５】

【発明の効果】以上説明したように，本発明によれば、高電圧印加時の圧電歪定数が大きく，かつ，比誘電率の温度変化が小さく，高温度範囲での電気抵抗率も大きいことから，広い温度範囲で安定な特性を有する圧電磁器材料を提供でき、アクチュエータ用材料として極めて有用である。

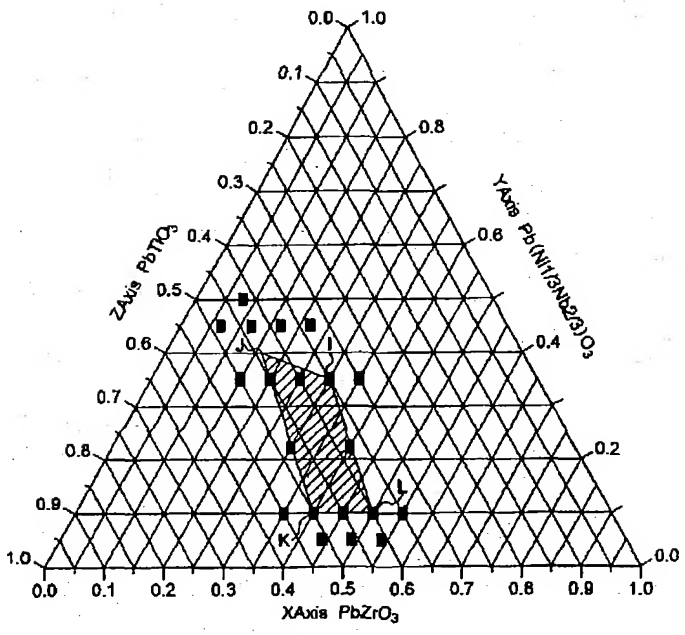
【図面の簡単な説明】

【図１】本発明の圧電磁器材料の組成範囲を三角座標で示す図である。

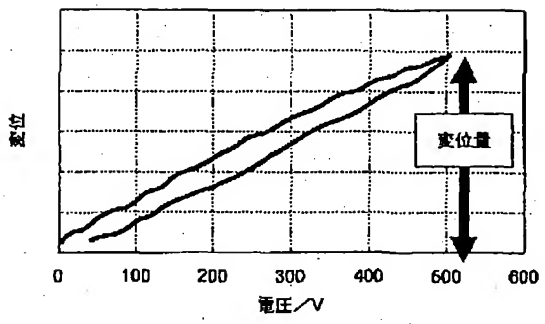
【図２】本発明の第１の実施の形態で示した，ｄ３３（５００ＫＶ）測定方法の概念を示す図であり，印加電圧と圧電変位の関係を示す図である。

【図３】本発明の第２の実施の形態で示した，ＭｎＯ添加量と，比抵抗の関係を示す図である。

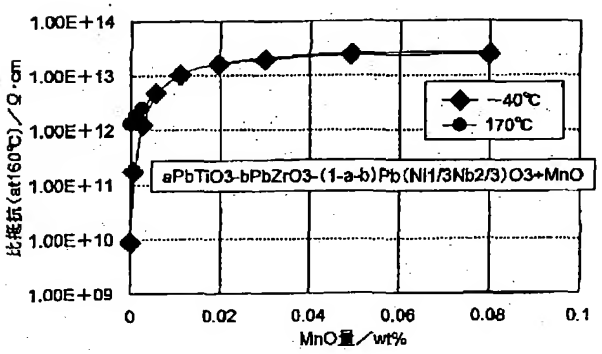
【図１】



【図２】



【図３】



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PIEZOELECTRIC CERAMIC COMPOSITION

Patent Number: JP2001302349
Publication date: 2001-10-31
Inventor(s): ISE OSAMU; MAMIYA YOICHI; KAWAKAMI
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IPC Classification: C04B35/49; H01L41/187
EC Classification:
Equivalents:

Abstract

PROBLEM TO BE SOLVED: To provide a piezoelectric ceramic composition having a large piezoelectric displacement particularly under high electric field, a small temperature change of a specific dielectric constant and an excellent insulation property.
SOLUTION: The piezoelectric ceramic composition is expressed by a composition formula, aPbTiO3+bPbZrO3+cPb(Ni1/3.Nb2/3)O3 (a+b+c=100), exists on a line formed by connecting composition points of point I (a=35 mol%, b=30 mol%, c=35 mol%), point J (a=44 mol%, b=16 mol%, c=40 mol%), point K (a=50 mol%, b=40 mol%, c=10 mol%) and point L (a=40 mol%, b=50 mol%, c=10 mol%) in fig. 1 and in the region surrounded by the 4 points and has >=500 pm/V piezoelectric displacement when 500 kV/m DC electric field is applied in the same direction as the polarization axis and <=300% temperature change of the specific dielectric constant in the temperature range of (-40)-170 deg.C.

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CLAIMS

[Claim(s)]
[Claim 1] Empirical formula aPbTiO3+bPbZrO3+cPb (nickel [1/3], Nb 2/3) I points which it is expressed with O3 (a+b+c=100) and the composition range shows to drawing 1 (a= 35-mol% and b= 30-mol% and c= 35-mol%), J point (a= 44-mol% and b= 16-mol% and c= 40-mol%), K points (a= 50-mol% and b= 40-mol% and c= 10-mol%), When it is the range made into the field surrounded by the line top which connects each L forming points (a= 40-mol% and b= 50-mol% and c= 10-mol%), and these four points and the direct-current electric field of 500 kV/m are impressed in the same direction as a polarization shaft The piezoelectric-ceramics constituent which the ****** displacement d33 (500kV) becomes 500 or more pm/V, and is characterized by the temperature change of specific inductive capacity being 300% or less in -40 degrees C - 170 degrees C.
[Claim 2] The piezoelectric-ceramics constituent which converts Mn into the oxide expressed with MnO to the total amount of a piezoelectric-ceramics constituent further in a piezoelectric-ceramics constituent according to claim 1, contains at a 0 - 0.05wt% (0 does not contain) rate, and is characterized by the specific resistance in -40 degrees C - 170 degrees C being 1.0x1011 or more ohm-cm.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] the thing about the piezoelectric-ceramics constituent with which this invention makes titanic-acid lead zirconate a principal component -- it is -- especially -- the piezo-electricity under high electric field -- a variation rate -- while an amount is large and the temperature change of specific inductive capacity is small, it is related with the piezoelectric-ceramics constituent excellent in insulation
[0002]
[Description of the Prior Art] Conventionally, as a piezoelectric-ceramics material, since a piezoelectric constant is size, the electrostrictive ceramics (it is hereafter called PZT system electrostrictive ceramics) which contains PbTiO3 and PbZrO3 as a principal component, and the multicomponent system PZT system electrostrictive ceramics which made compound perovskites dissolve as the third fourth component are widely used as a material for actuators by making a piezoelectric transducer into the start. the piezoelectric-ceramics material of these systems -- general -- composition near the mol photograph pick phase boundary (MPB) -- setting -- piezo-electricity, such as a piezoelectric constant (d constant), -- since the property which contributes to a variation rate improves, piezoelectric-ceramics material of composition near the MPB is widely put in practical use by the charge of actuator material
[0003]
[Problem(s) to be Solved by the Invention] however, the value calculated by the resonance-antiresonating method by which the aforementioned piezoelectric constant was generally shown in the EMAS-6100 grade -- it is -- fundamental -- the piezo-electricity at the time of low electric-field (about 100 V/m of divisors) impression -- the rate of a variation rate is shown On the other hand, the drive electric field in an actual electrostrictive actuator may also become hundreds kV/m - thousands kV/m, and may not have a meaning with the practical piezoelectric constant for which it asked by the aforementioned method.
[0004] Furthermore, in connection with the breadth of the electrostrictive actuator use range, the property stability in a latus temperature requirement, especially the temperature stability of electrostatic capacity are called for in recent years. For example, when an electrostrictive actuator is used as parts for automobiles, according to the operating environment, the property stability in the latus temperature requirement which becomes -40 degrees C - no less than 170 degrees C may be required. On the other hand, generally, temperature change of specific inductive capacity became large, and the problem has produced the piezoelectric-ceramics material in the aforementioned composition near the MPB at the stability of the actuator property in a latus temperature requirement, especially the stability of electrostatic capacity. Since d constant is large, the piezoelectric-ceramics constituent of PbTiO3-PbZrO3-Pb(nickel1/3Nb 2/3) O3 system (it is hereafter called a PNN-PZT system) is used as a piezoelectric-ceramics material for AKUYUETA elements. However, the piezoelectric-ceramics material of this system has comparatively small electrical resistivity, when much more thickness uses it for the element around 100 micrometers like a laminating type piezoelectric device, voltage which can

be impressed could not be enlarged, but sufficient property cannot be pulled out or the trouble of carrying out dielectric breakdown during use has produced it.
[0005] Moreover, since the temperature change of electrical resistivity of the aforementioned PNN-PZT system piezoelectric-ceramics material was also large, when using it by the above latus temperature requirements especially, it had the problem of reliability falling further.
[0006] Then, since the piezo-electric distorted constant at the time of high-voltage impression is large, and the temperature change of specific inductive capacity is small and the electrical resistivity in the high temperature range is also large, the general technical technical problem of this invention is to offer the piezoelectric-ceramics constituent which has a stable property by the latus temperature requirement.
[0007] Moreover, the special technical technical problem of this invention becomes substantial from the aforementioned piezoelectric-ceramics constituent, and is to offer a piezoelectric-ceramics constituent useful as a charge of actuator material.
[0008]
[Means for Solving the Problem] this invention person Empirical-formula aPbTiO3+bPbZrO3+cPb O3 (nickel1/3Nb 2/3) As a result of investigating various properties, d33 (500kV) becomes 500 or more pm/V in a field predetermined in the composition range. the piezo-electricity of a piezoelectric-ceramics constituent expressed with (a+b+c=100) -- a variation rate -- in -40 degrees C - 170 degrees C The temperature change of specific inductive capacity finds out 300% or less and a bird clapper, and it comes to succeed in this invention.
[0009] Moreover, by converting Mn into the oxide expressed with MnO to the above-mentioned piezoelectric-ceramics constituent, and containing at a 0 - 0.05wt% (0 not containing) rate, it finds out that the insulation of the above-mentioned piezoelectric-ceramics constituent improves, and comes to succeed in this invention.
[0010] Namely, I points which according to this invention it is expressed with empirical-formula aPbTiO3+bPbZrO3+cPb(nickel 1/3, Nb 2/3) O3 (a+b+c=100), and the composition range shows to drawing 1 (a= 35-mol% and b= 30-mol% and c= 35-mol%), J point (a= 44-mol% and b= 16-mol% and c= 40-mol%), K points (a= 50-mol% and b= 40-mol% and c= 10-mol%), When it is the range made into the field surrounded by the line top which connects each L forming points (a= 40-mol% and b= 50-mol% and c= 10-mol%), and these four points and the direct-current electric field of 500 kV/m are impressed in the same direction as a polarization shaft The piezoelectric-ceramics constituent which the ****** displacement d33 (500kV) becomes 500 or more pm/V, and is characterized by the temperature change of specific inductive capacity being 300% or less in -40 degrees C - 170 degrees C is obtained.
[0011] Moreover, according to this invention, in the aforementioned piezoelectric-ceramics constituent, Mn is further converted into the oxide expressed with MnO to the total amount of a piezoelectric-ceramics constituent, it contains at a 0 - 0.05wt% (0 does not contain) rate, and the piezoelectric-ceramics constituent characterized by the specific resistance in -40 degrees C - 170 degrees C being 1.0x1011 or more ohm-cm is obtained.
[0012]
[Embodiments of the Invention] First, this invention is explained with reference to a drawing.
[0013] Drawing 1 is drawing having shown the composition range of the piezoelectric-ceramics constituent of this invention by the triangular coordinate. As shown in drawing 1 , the piezoelectric-ceramics constituent of this invention I points (a= 35-mol% and b= 30-mol% and c= 35-mol%), J point (a= 44-mol% and b= 16-mol% and c= 40-mol%), It has the composition of the range made into the field surrounded by the line top which connects K points (a= 50-mol% and b= 40-mol% and c= 10-mol%) and L forming points (a= 40-mol% and b= 50-mol% and c= 10-mol%), and these four points. piezo-electricity when the piezoelectric-ceramics constituent of this invention impresses the direct-current electric field of 500 kV/m in the same direction as a polarization shaft in this composition -- a variation rate d33 (500kV) becomes 500 or more pm/V, and the range of it is -40 degrees C - 170 degrees C, and the temperature change of specific inductive capacity has 300% or less of property
[0014] Furthermore, the piezo-electric constituent of this invention converts Mn into the oxide expressed with MnO to the total amount of a piezoelectric-ceramics constituent further in the

aforementioned piezoelectric-ceramics constituent, and contains it at a 0 - 0.05wt% (0 does not contain) rate, and the specific resistance in -40 degrees C - 170 degrees C has the property of 1.0x1011 or more ohm-cm by this.

[0015] Next, the gestalt of operation of this invention is explained.

[0016] (Gestalt of the 1st operation) Weighing capacity of the raw material of a lead oxide (PbO), titanium oxide (PbO), a zirconium oxide (ZrO2), nickel oxide (NiO), and a niobium oxide (Nb 2O5) was carried out so that it might be set to chemical formula aPbTiO3-bPbZrO3-cPb(nickel1/3Nb 2/3) O3, and with the zirconia ball, such raw material powder was put in into the acrylic pot, and carried out wet blending for 20 hours. Next, after performing **** for these mixed powder in alumina ****** after dehydration dryness, wet grinding of each ****** was carried out with the zirconia ball in an acrylic pot for 15 hours. Then, the binder was mixed to the **** pulverized powder obtained by carrying out dehydration dryness, it was pressurized, and it fabricated to diameter (phi) 15x thickness (T)3mm. After calcinating this Plastic solid at 1100 degrees C - 1300 degrees C for 2 hours and processing each sintered compact into the thickness of 1mm, it considered as the sample from which composition differs, respectively by applying a silver paste to both sides, printing at 450 degrees C, and forming an electrode. Thus, polarization processing was carried out for each obtained sample by mm in 3kV /, ~~HP4194A and the thermostat were used, and the 1kHz temperature characteristic of specific-inductive-~~ capacity epsilonr was measured. After holding the temperature characteristic 5 degrees C - every 10 degrees C in -40 degrees C - 400 degrees C for 30 minutes, it measured 1kHz epsilonr in each temperature. Moreover, d33 (500kV) impressed the voltage of 0V ->500V ->0V to the aforementioned sample supported in the central point in uniform velocity and 2 seconds, and measured and computed the variation rate of the sample thickness direction using the fringe counter formula laser displacement gage.

[0017] Drawing 2 is drawing showing the example of measurement of d33 (500kV). it is shown in drawing 2 -- as -- a measurement sample with a thickness of 1mm -- the variation rate at the time of direct-current-voltage impression of 500V (field strength 500 kV/m) -- d33 (500kV) was computed from the amount

[0018] Moreover, the rate of a temperature change of -40 degrees C - 170 degrees' C epsilonr is shown with d33 (500kV) in each forming point in the following table 1. Sample No. which attached table 1 Naka "*" shows the outside of the range of this invention.

[0019]

[Table 1]

各組成点における圧電磁器材料の特性

	試料 No.	各成分			d_{33}(500KV)/ pm·V^{-1}	Δεr	Tc(℃)
		a	b	c			
*	1	43	12	45	530	500%	180
	2	44	16	40	670	170%	200
*	3	39	21	40	1250	550%	190
*	4	50	15	35	450	170%	230
	5	45	20	35	530	180%	220
	6	40	25	35	1000	230%	210
	7	35	30	35	800	280%	200
*	8	30	35	35	700	700%	190
	9	47.5	30	22.5	520	160%	270
	10	37.5	40	22.5	750	290%	250
*	11	55	35	10	470	150%	340
	12	50	40	10	520	160%	330
	13	45	45	10	700	170%	320
	14	40	50	10	600	270%	310
*	15	35	55	10	520	700%	300
*	16	51	44	5	420	160%	350
*	17	46	49	5	480	190%	340
*	18	41	54	5	400	280%	330

備考)＊印は本発明の範囲外

The following things can be read from the above-mentioned table 1. That is, in sample No.1, and 3 and 8, since the Curie temperature (Tc) of a piezoelectric-ceramics constituent becomes 200 degrees C or less and the temperature change of -40 degrees C - 170 degrees C epsilonr exceeds 300%, it is not contained in the range of this invention.

[0020] moreover, the line which connects sample No.7, and 10 and 14 -- PbZrO3 -- in a rich field, d33 [comparatively high] (500kV) is obtained -- **** -- since the temperature change of ****** and epsilonr becomes very large, it is not contained in the range of this invention

[0021] Moreover, since the value of d33 (500kV) becomes less than 500 pm/V, sample No.4, and 11, 16, 17 and 18 are not contained in the range of this invention, respectively.

[0022] From these results, the property made into the target of this invention Sample No.2, and 7, 12 and 14 respectively No.2 (a= 44-mol% and b= 16-mol% and c= 40-mol%), No.7 (a= 35-mol% and b= 30-mol% and c= 35-mol%), In the range made into the field surrounded by the line top which connects No.12 (a= 50-mol% and b= 40-mol% and c= 10-mol%) and the forming point of No.14 (a= 40-mol% and b= 50-mol% and c= 10-mol%), and these four points It turns out that it is attained in the field surrounded by four square shapes shown in drawing 1 .

[0023] A lead oxide (PbO), titanium oxide (TiO2), (Gestalt of the 2nd operation) A zirconium oxide (ZrO2), nickel oxide (NiO), a niobium oxide (Nb 2O5), The raw material of manganese carbonate (MnCO3) so that it may be set to chemical formula aPbTiO3-bPbZrO3-CPb(nickel1/3Nb 2/3) O3+MnO (wt%) Weighing capacity was carried out and the specific resistance of the sample which created and created the sample by the same method as the gestalt of the 1st operation which comes out 170 degrees C -40 degrees C, respectively was measured.

[0024] An example of the result is shown in drawing 3 . the constant temperature from drawing 3 -- in a field, although specific resistance falls, it turns out that specific resistance improves notably and is satisfied [only with carrying out ultralow-volume addition of the MnO] of the desired value of this invention Moreover, when the addition of MnO exceeded 0.05wt%, it turns out that the improvement effect in specific resistance beyond it can be desired, and there is nothing. For a certain reason, superfluous addition of MnO can also judge the inclination to degrade piezo-electric properties, such as

a piezoelectric constant, that less than [0.05wt%] is a suitable value to the target of this invention.
[0025]
[Effect of the Invention] Since according to this invention the piezo-electric distorted constant at the time of high-voltage impression is large, and the temperature change of specific inductive capacity is small and the electrical resistivity in the high temperature range is also large as explained above, the piezoelectric-ceramics material which has a stable property can be offered, and it is very useful as a charge of actuator material at a latus temperature requirement.

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PRIOR ART

[Description of the Prior Art] Conventionally, as a piezoelectric-ceramics material, since a piezoelectric constant is size, the electrostrictive ceramics (it is hereafter called PZT system electrostrictive ceramics) which contains PbTiO3 and PbZrO3 as a principal component, and the multicomponent system PZT system electrostrictive ceramics which made compound perovskites dissolve as the third fourth component are widely used as a material for actuators by making a piezoelectric transducer into the start. the piezoelectric-ceramics material of these systems -- general -- composition near the mol photograph pick phase boundary (MPB) -- setting -- piezo-electricity, such as a piezoelectric constant (d constant), -- since the property which contributes to a variation rate improves, piezoelectric-ceramics material of composition near the MPB is widely put in practical use by the charge of actuator material

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is drawing showing the composition range of the piezoelectric-ceramics material of this invention by the triangular coordinate.
[Drawing 2] It is drawing which was shown with the gestalt of operation of the 1st of this invention and in which showing the concept of d33 (500kV) measuring method, and is drawing showing the relation of the piezo-electric displacement by applied voltage.
[Drawing 3] It is drawing showing the relation of specific resistance with the MnO addition shown with the gestalt of operation of the 2nd of this invention.

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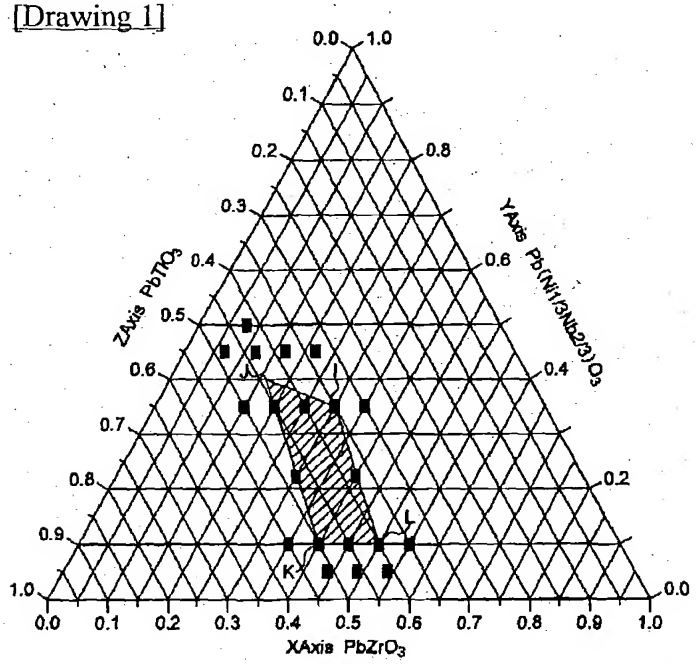
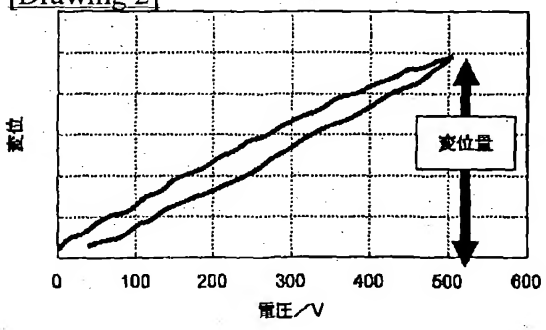
DRAWINGS

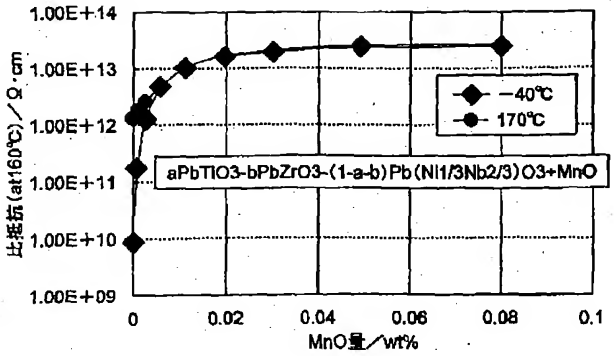
[Drawing 1]



[Drawing 2]



[Drawing 3]



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